BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 992—996 (1968)

# Solvent Effect under High Pressure. II⁽¹⁾

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(Received October 19, 1967)

The activation volume of the reaction of triethylamine with ethyl iodide has been measured in four solvents. A linear relationship has been observed between the values of $\Delta V_0^{\neq}$ for the Menschutkin reaction in various solvents and the products of the compressibility and the molar volume of the pure solvent, as has been suggested in a previous paper. From the slope of the plots of $(-\Delta V_0^{\neq})$ *vs.* $KV^{\circ}$, the product of the solvation number and the average pressure within the solvation shell of an activated complex has been calculated to be $2.6\times10^3$ (kg·cm$^{-2}$) according to a model proposed by the authors. An abnormal acceleration due to pressure has been observed for the reaction of triethylamine with ethyl iodide in *p*-xylene and dioxane at 30°C. This acceleration effects has been attributed to the partial freezing of the solvent under high pressure.

A study of the effects of solvents on an activation volume would throw some light on the effects of solvents on reaction rates and mechanisms.

In a previous report⁽¹⁾ the present authors proposed a relation between the activation volumes in a variety of solvents and the compressibilities of the solvents on the basis of the electrostriction theory. In the present paper, it will be established that the expression then proposed by the authors is useful for the description of the variation in the activation volumes for the reaction of triethylamine with ethyl iodide and of pyridine with methyl iodide⁽²⁾ upon a change of solvents.

An abnormal acceleration effect of the rates of the Menschutkin reaction due to pressure was reported by the present authors in the previous paper.⁽¹⁾ Compared with the results of the reaction rates in frozen solutions obtained by Pincock *et al.*,⁽³⁾ this abnormal acceleration due to pressure has been attributed to the partial freezing of the solution resulting from the rize of the freezing point with an increase in the pressure. In order to establish this phenomenon further, the same reaction has been treated in dioxane and *p*-xylene solvents under high pressures.

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1) Part I: Y. Kondo, H. Tojima and N. Tokura, This Bulletin, **40**, 1408 (1967).

2) H. Hartmann, H. Kelm and G. Rinck, *Z. physik. Chem. N. F.*, **44**, 335 (1965).

3) R. E. Pincock and T. E. Kiovsky, *J. Am. Chem. Soc.*, **88**, 51 (1966).

## Experimental

**Materials.** Triethylamine and ethyl iodide were purified by a method described earlier.1) The solvents used were purified by known methods.4)

**Apparatus and Kinetic Procedure.** The apparatus for kinetic runs under high pressure used in this experiment is that described in the previous paper.1) As the reaction product, tetraethylammonium iodide, is insoluble in the solvents used in this experiment, the reaction rates were measured by batch processes with the use of polyethylene ampoules.

The activation volumes were evaluated by the graphical method developed by the authors, using Eqs. (1) and (2):

$$\log(k_p/k_1) = AP + BP^2 \qquad (1)$$

$$\Delta V_0^{\neq} = -2.303\,A\boldsymbol{RT} \qquad (2)$$

Typical runs under high pressures are represented in Table 1, while an example of the plot of $\log(k_p/k_1)/P$ *vs.* $P$ is shown in Fig. 1.

The coefficients, $A$ and $B$, of Eq. (1) for the reactions in various solvents are represented in Table 2.

TABLE 1. RATE CONSTANTS UNDER HIGH PRESSURES
Reaction: $(C_2H_5)_3N + C_2H_5I$, Solvent: *p*-Xylene
Reaction temp.: 45°C

| $P$ kg·cm$^{-2}$ | $k_p \times 10^5$ $l$ mol$^{-1}$ sec$^{-1}$ | $k_p/k_1$ | $\{\log(k_p/k_1)/P\} \times 10^4$ kg$^{-1}$ cm$^2$ |
|---|---|---|---|
| 1 | 0.6930 | 1 | |
| 300 | 1.135 | 1.638 | 7.143 |
| 300 | 1.201 | 1.733 | 7.960 |
| 600 | 1.880 | 2.713 | 7.223 |
| 900 | 2.733 | 3.944 | 6.621 |
| 900 | 2.748 | 3.965 | 6.647 |
| 1200 | 3.920 | 5.657 | 6.272 |
| 1500 | 5.425 | 7.828 | 5.958 |
| 1500 | 5.509 | 7.949 | 6.000 |

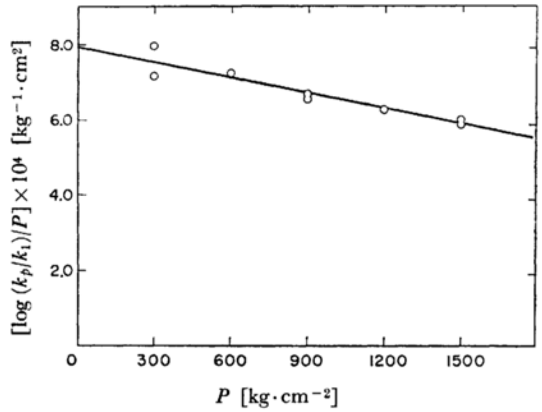

Fig. 1. Plot of $\log(k_p/k_1)/P$ *vs.* $P$ for the reaction of ethyl iodide with triethylamine in *p*-xylene at 45°C.

TABLE 2. COEFFICIENTS, $A$ AND $B$, OF EQ. (1)
Reaction: $(C_2H_5)_3N + C_2H_5I$

| Solvent | Reaction temp., °C | $A$ kg$^{-1}$·cm$^2$ | $B$ kg$^{-2}$·cm$^4$ |
|---|---|---|---|
| *p*-Xylene | 45 | $7.93 \times 10^{-4}$ | $-1.34 \times 10^{-7}$ |
| Dioxane | 45 | $6.52 \times 10^{-4}$ | $-8.54 \times 10^{-8}$ |
| Bromobenzene | 25 | $6.15 \times 10^{-4}$ | $-8.47 \times 10^{-8}$ |
| Chlorobenzene | 25 | $6.50 \times 10^{-4}$ | $-1.06 \times 10^{-7}$ |

## Results and Discussion

**A Solvent Effect on an Activation Volume.** Recently, the relationship between the thermodynamic activation parameters and the dielectric properties of the medium, considered as a continuum, has been discussed by Hartmann and his collaborators.2,5,6)

In the previous report1) the following expression for the effects of solvents on the activation volumes of the Menschutkin reaction has been derived on the basis of the assumption that the partial molar volume of the activated complex is expressed as a function of the molar volume of a pure activated complex and the electrostriction of a solvent molecule surrounding an activated complex, while the partial molar volume of a reactant is independent of the nature of the solvent:

$$\Delta V_0^{\neq} = \{V_{\neq} - (\overline{V}_A^\circ + \overline{V}_B^\circ)\} - ZKV^\circ \Delta P \qquad (3)$$

In Eq. (3), $V_{\neq}$, $\overline{V}_A^\circ$, $\overline{V}_B^\circ$, $Z$, $K$, $V^\circ$, and $\Delta P$ stand for the molar volume of an activated complex in its pure state; the partial molar volume of the reactants, A and B; the solvation number of an activated complex; the compressibility and the molar volume of a pure solvent, and the average pressure within the solvation shell of an activated complex respectively.

The activation volumes obtained by the authors are represented in Table 3.

In Fig. 2 the activation volumes for the reaction of triethylamine with ethyl iodide and those for the reaction of pyridine with methyl iodide2) are plotted against the values for $KV^\circ$ at 25°C.

For these two reactions there exists a similar correlation between the values for $\Delta V_0^{\neq}$ and those for $KV^\circ$; in addition, the slopes of the lines, *i. e.*, the values for $Z \cdot \Delta P$, are like one another.

Since the values for $Z \cdot \Delta P$ stand for the product of the solvation number and the average pressure within the solvation shell of an activated complex, these values will vary depending on the structure of the activated complex or on the degree of the development of ionic charges during the course of the reaction, *i. e.*, on whether the ionic charges developed or decrease as the reaction proceeds.

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4) "Technique of Organic Chemistry. VII. Organic Solvents," ed. by A. Weissberger, Interscience, New York (1955).

5) H. Heydtmann, A. P. Schmidt and H. Hartmann, *Ber. Bunsenges. physik. Chem.*, **70**, 444 (1966).

6) H. Heydtmann, *Z. physik. Chem. N. F.*, **54**, 237 (1967).

TABLE 3. ACTIVATION VOLUMES AND COMPRESSIBILITIES OF THE SOLVENTS
Reaction: $(C_2H_5)_3N + C_2H_5I$

| Solvent | Reaction temp. °C | $A\times10^4$ $cm^2\cdot kg^{-1}$ | $KV^\circ\times10^9$ [7] $cm^5\cdot dyn^{-1}\cdot mol^{-1}$ | $-\Delta V_0^{\ddagger}$ $ml\cdot mol^{-1}$ |
|---|---|---|---|---|
| *p*-Xylene | 45 | 7.93 | 12.52* | 49.3 |
| Dioxane | 45 | 6.52 | — | 40.5 |
| Bromobenzene | 25 | 6.15 | 7.05 | 35.8 |
| Chlorobenzene | 25 | 6.50 | 7.67 | 37.8 |
| MeOH[1] | 25 | 5.50 | 5.12 | 32.0 |
| Nitrobenzene[1] | 25 | 5.16 | 5.17 | 30.0 |
| Benzene[1] | 25 | 7.47 | 8.65 | 43.5 |

* The value for a compressibility, *K*, is that of *m*-xylene at 45°C.

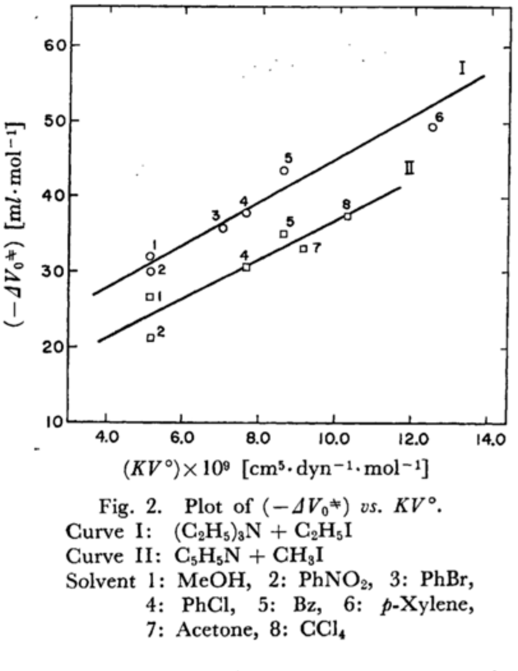

Fig. 2. Plot of $(-\Delta V_0^{\ddagger})$ *vs.* $KV^\circ$.
Curve I: $(C_2H_5)_3N + C_2H_5I$
Curve II: $C_5H_5N + CH_3I$
Solvent 1: MeOH, 2: $PhNO_2$, 3: PhBr, 4: PhCl, 5: Bz, 6: *p*-Xylene, 7: Acetone, 8: $CCl_4$

The values of $Z\cdot\Delta P$ for these two reactions, calculated from the slopes of Fig. 2, are about $2.6\times10^3$ ($kg\cdot cm^{-2}$).

If we assume that the solvation number, *Z*, is equal to eight according to the theory of a nonelectrolyte solution[8] or the solvation number of the quaternary ammonium salt in liquid sulfur dioxide measured earlier by the present authers,[9] a value of approximately 320 ($kg\cdot cm^{-2}$) is obtained for the average pressure within the solvation shell of an activated complex.

In the estimation of the amount of the hydration of an electrolyte, the hydrated water within the hydration shell is assumed to be incompressible.[10]

The average pressure within the hydration shell of the alkali metal halides is calculated to be approximately 4300 ($kg\cdot cm^{-2}$) from the measurement of the density and of the ultrasonic velocity in an electrolyte solution.[11]

The comparison of these results suggests that the activated complex is solvated to a lower extent than the ions of the reaction products.

Generally, $\Delta V_0^{\ddagger}$ has been treated as the sum of the two terms:[12]

$$\Delta V_0^{\ddagger} = \Delta V_1^{\ddagger} + \Delta V_2^{\ddagger} \tag{4}$$

where $\Delta V_1^{\ddagger}$ is the change in the volume of the reacting particles during the formation of an activated complex and $\Delta V_2^{\ddagger}$ is the change in the volume of the solvent, resulting from the formation of the activated complex.

Since, in the model proposed by the authors, the first term on the right-hand side of Eq. (3) is independent of the nature of the solvent, whereas the second term is dependent, the former should correspond to the first term on the right-hand side of Eq. (4), whereas the latter should correspond to the second term.

Then, the value of $\Delta V_0^{\ddagger}$ obtained by extrapolating to zero the value of $KV^\circ$ should represent $\Delta V_1^{\ddagger}$, *i. e.*, the volume change of the reacting particles themselves.

Since the activation volume calculated on the basis of the Gonikberg model[13] should give the values of $\Delta V_1^{\ddagger}$ in Eq. (4), these values should correspond to the first term of Eq. (3), obtained by extrapolation.

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[7] C. D. Hodgmann, "Handbook of Chemistry and Physics," 44th Ed., Chemical Rubber Publishing Co., Cleveland (1962), pp. 2212—2218.

[8] J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Englewood Cliffs, N. J. (1962).

[9] Y. Kondo, T. Goto, I. Suo and N. Tokura, This Bulletin, **36**, 1230 (1966).

[10] J. O'M. Bockris, "Modern Aspects of Electrochemistry," Butterworths Scientific Publications, London (1954).

[11] T. Yasunaga and T. Sasaki, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **72**, 89 (1957).

[12] S. D. Hamann, "Physico-Chemical Effects of Pressure," Butterworths Scientific Publications, London (1957).

[13] M. G. Gonikberg, "Chemical Equilibria and Reaction Rates at High Pressures," 2nd Ed., Israel Program for Scientific Translations, Jerusalem (1963).

The values of $\Delta V_1^{\neq}$ extrapolated by the least-mean-square method from the experimental results shown in Fig. 2 are compared with the values calculated by Gonikberg *et al.,* in Table 4.

TABLE 4. THE VALUES OF $\Delta V_1^{\neq}$

| Reaction | $\Delta V_1^{\neq}$ (Extrapolated) $ml\cdot mol^{-1}$ | $\Delta V_1^{\neq}$ (Calcd by Gonikberg[13)]) $ml\cdot mol^{-1}$ |
|---|---|---|
| $C_5H_5N + CH_3I$ | $-10.7$ | $-9$ |
| $(C_2H_5)_3N + C_2H_5I$ | $-18.4$ | $-24$* |

* The value for the reaction of triethylamine with isopropyl iodide.

It has been established that, for the reaction of pyridine with methyl iodide, the activation volume obtained by extrapolation is nearly equal to the calculated value.

Therefore, the extrapolation method mentioned above will be useful in resolving the values of $\Delta V_0^{\neq}$ measured in various solvents into their components, *i. e.,* $\Delta V_1^{\neq}$ and $\Delta V_2^{\neq}$, definitely.

**An Abnormal Acceleration under High Pressure.** In their previous study[1)] the authors observed a greater acceleration effect of pressure for the rates of the Menschutkin reaction in benzene and nitrobenzene than was expected from the power-series treatment.

After being compared with the results of the reaction rates in frozen solutions by Pincock *et al.,*[3)] this acceleration effect has been attributed to the partial freezing of the solvent which results from the rise in the freezing point with an increase in an external pressure.[1)]

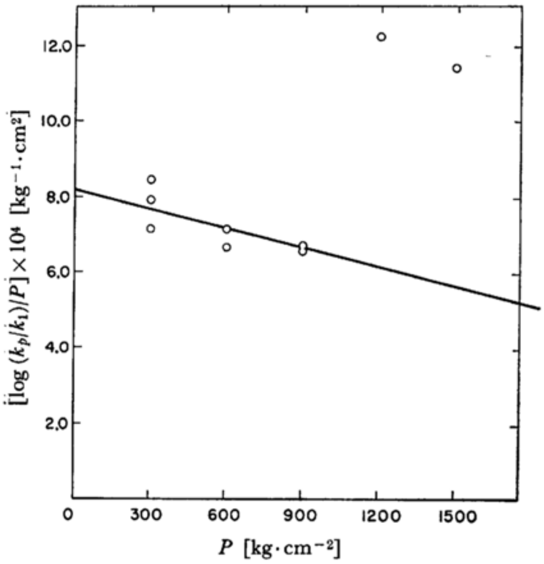

Fig. 3. Deviation from the linear relation between $\log(k_p/k_1)/P$ and $P$ for the reaction of ethyl iodide with triethylamine in *p*-xylene at 30°C.

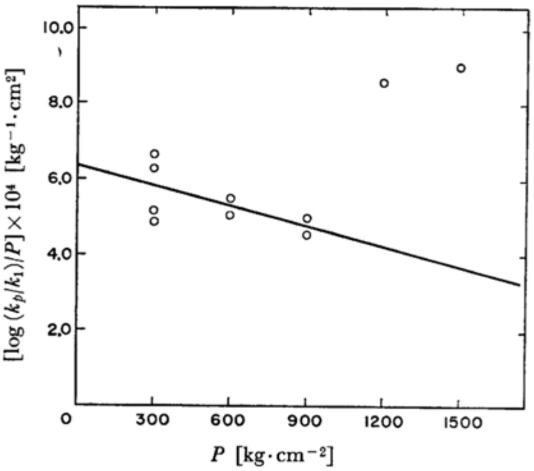

Fig. 4. Deviation from the linear relation between $\log(k_p/k_1)/P$ and $P$ for the reaction of ethyl iodide with triethylamine in dioxane at 30°C.

In the previous study the experimental results in a high-temperature region were referred to the literature. With the object of obtaining the rate constants in both the low and high temperature regions; for the former the abnormal acceleration should be observed, but for the latter the plots of $\log(k_p/k_1)/P$ *vs.* $P$ should be linear, the effects of the pressure on the rate constants of the Menschutkin reaction have been measured in two solvents, dioxane and *p*-xylene.

For the rate constants at 30°C large deviations from the linear relations of $\log(k_p/k_1)/P$ with the pressure have been found at the pressures of both 1200 and 1500 ($kg\cdot cm^{-2}$) (see Figs. 3 and 4).

If this acceleration is caused by a freezing of the solvent similar to the phenomenon found by Pincock *et al.,*[3)] the freezing points of these solvents at 1200 and 1500 ($kg\cdot cm^{-2}$) should lie several degrees above the experimental temperature, *i. e.,* 30°C.

If we assume that the volume change on fusion per mole of a solvent, $\Delta V_f$, is equal to ten percent of the molar volume of a pure solvent, on the basis of Eq.(5):

$$\left(\frac{dP}{dT}\right) = \left(\frac{\Delta H_f}{T\Delta V_f}\right) \tag{5}$$

the freezing points at 1000 ($kg\cdot cm^{-2}$) are calculated to be 34°C and 30°C for *p*-xylene and dioxane respectively.

Therefore, in the region where the abnormal acceleration has been observed, *i. e.,* at 1200 and 1500 ($kg\cdot cm^{-2}$), moderate portions of the solvent would be frozen.

Pincock *et al.*[3)] examined the reaction of triethylamine with methyl iodide in frozen benzene solutions; they found that the reaction is accelerated moderately and that the reaction in a frozen solution becomes a first-order reaction, in contrast to the second order in an unfrozen solution. They were able to explain their findings quantitatively by taking into account the fact that, if the reactants are soluble enough when the equilibrium is reached at a temperature above the eutectic temperature of the system, the reactants are rejected by the solid phase and become more concentrated in the unfrozen liquid region, and the fact that since, in this reaction, the reaction product, quaternary ammonium iodide, is insoluble in the solution, the walls of the reaction regions close in to hold the concentration of the remaining solute at a constant value.[3]

As the reaction product of triethylamine with ethyl iodide, tetraethylammonium iodide, is almost insoluble in the solvents used in this experiment, the systems treated by the authors are similar to the system studied by Pincock *et al.*[3]

The plots of log (concentration) against the time gave good straight lines for the reactions in the two solvents at the pressures of 1200 and 1500 (kg·cm$^{-2}$) (see Figs. 5 and 6).

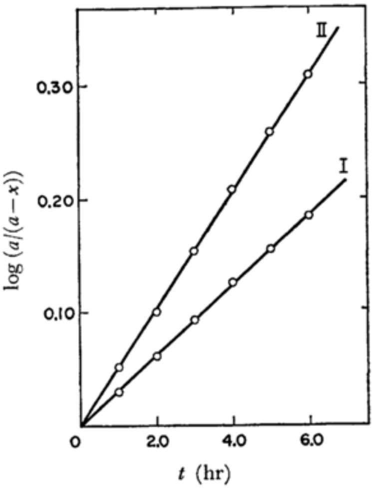

Fig. 5. First order plot for the reaction of ethyl iodide with triethylamine in $p$-xylene under high pressure at 30°C.
Curve I: at 1200 [kg·cm$^{-2}$]
II: at 1500 [kg·cm$^{-2}$]

However, at these pressures the plots of the reciprocal concentrations against the time were distinctly curved with equal concentrations of the reactants.

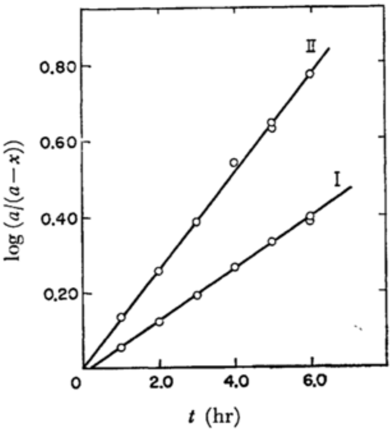

Fig. 6. First order plot for the reaction of ethyl iodide with triethylamine in dioxane under high pressure at 30°C.
Curve I: at 1200 [kg·cm$^{-2}$]
II: at 1500 [kg·cm$^{-2}$]

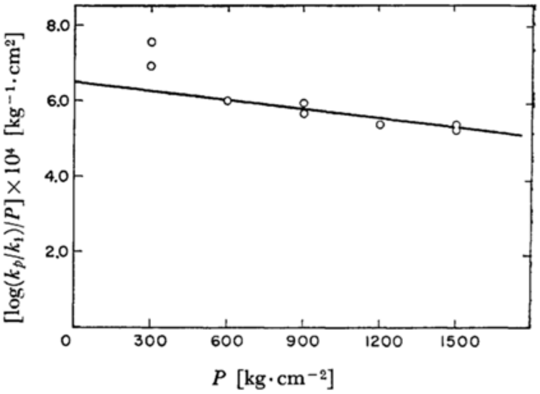

Fig. 7. Plot of $\log(k_p/k_1)/P$ *vs.* $P$ for the reaction of ethyl iodide with triethylamine in dioxane at 45°C.

The linear correlation can be expected to hold between $\log(k_p/k_1)/P$ and $P$ over the region where no anomalous behavior such as the freezing of a solvent could be encountered at all.

The rate constants measured at a relatively high temperature, *i. e.*, 45°C, where the freezing of the solvent could not be expected even under the added pressures, show good correlations between $\log(k_p/k_1)/P$ and pressure (see Figs. 7 and 1).

The facts mentioned above support the view that the abnormal acceleration observed in this experiment can be attributed to the freezing of the solvent under high pressures.